

# Crystal structures and magnetic order of $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$ ( $\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$ ): Possible orbital glass ferromagnetic state

E. Granado,<sup>1,2,\*</sup> Q. Huang,<sup>3</sup> J. W. Lynn,<sup>3,4</sup> J. Gopalakrishnan,<sup>4,5</sup> and K. Ramesha<sup>5</sup><sup>1</sup>*Instituto de Física “Gleb Wataghin,” UNICAMP, Caixa Postal 6165, Campinas, SP, CEP 13083-970, Brazil*<sup>2</sup>*Laboratório Nacional de Luz Síncrotron, Caixa Postal 6192, Campinas, SP, CEP 13084-971, Brazil*<sup>3</sup>*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*<sup>4</sup>*Center for Superconductivity Research, University of Maryland, College Park, Maryland 20742, USA*<sup>5</sup>*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*

(Received 30 August 2004; published 17 December 2004)

The crystallographic and magnetic properties of  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$ ) were investigated by means of neutron powder diffraction. All studied samples show the orthorhombic perovskite crystal structure, space group  $Pnma$ , with regular  $(\text{Mn}, \text{Ru})\text{O}_6$  octahedra and no chemical ordering of the  $\text{Mn}^{3+}$  and  $\text{Ru}^{4+}$  ions. Ferromagnetic spin structures were observed below  $T_c \sim 200\text{--}250$  K, with an average ordered moment of  $\sim 1.8\text{--}2.0\mu_B/(\text{Mn}, \text{Ru})$ . The observation of long-range ferromagnetism and the absence of orbital ordering are rationalized in terms of a strong Mn—Ru hybridization, which may freeze the orbital degree of freedom and broaden the  $e_g$  valence band, leading to an orbital glass state with carrier-mediated ferromagnetism.

DOI: 10.1103/PhysRevB.70.214416

PACS number(s): 75.25.+z, 61.12.Ld, 75.50.Dd, 75.47.Lx

## I. INTRODUCTION

The large variety of interesting physical phenomena observed in manganese perovskites has motivated intensive investigations on the phase diagrams of these compounds as functions of chemical doping, temperature, pressure, magnetic field, and lattice mismatch, among other variables. Particularly, a number of recent works have dealt with dilution of transition-metal impurities at the Mn crystallographic site.<sup>1–3</sup> The main focus has been on the influence of such impurities on the relative strength of the ferromagnetic (FM) double exchange interactions against the competing tendency for charge and orbital ordering of the  $\text{Mn}^{3+}:e_g$  electrons. Less work has been performed in compounds with large levels ( $>20\%$ ) of transition-metal substitution. For 50% substitution, such mixed systems may be classified as double perovskites, with possible transition-metal chemical ordering.<sup>4</sup>

The particular case of Ru substitution in manganites appears to yield interesting effects. It is believed that such ions may be present in either low-spin  $\text{Ru}^{4+}$  ( $4d:t_{2g}^4$ ) or  $\text{Ru}^{5+}$  ( $4d:t_{2g}^3$ ) electronic configurations, and are substantially more covalent than the  $3d$  ions. Previous works indicate that light Ru substitution strongly favors the ferromagnetic metallic (FMM) states.<sup>1–3,5</sup> This is opposite to the general trend observed for other transition-metal substitutions in manganites, where the  $B$ -site disorder tends to disrupt the conduction and exchange paths, suppressing the FMM state.<sup>1</sup> Despite these interesting results, relatively few details are presently known about the magnetism of heavily Ru-substituted manganites, as well as on its possible coupling with the lattice degrees of freedom.

In this work, the crystal and magnetic structures of  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$ ) are investigated by means of high-resolution neutron powder diffraction (NPD). All samples crystallize in an orthorhombic perovskite structure, with no chemical ordering of Mn and Ru

ions. The  $(\text{Mn}, \text{Ru})\text{O}_6$  octahedra are regular, and the Mn—O—Mn bonding angles increase substantially from  $\text{A}=\text{Ca}$  to  $\text{Ba}$ . Long-range FM structures of  $(\text{Mn}, \text{Ru})$  spins were observed below  $T_c \sim 200\text{--}250$  K, with no evidence of coexisting antiferromagnetic order parameters. The average ordered moment per transition-metal ion at 10 K is  $\sim 1.8\text{--}2.0\mu_B/(\text{Mn}, \text{Ru})$ , substantially smaller than the  $\sim 3\mu_B/(\text{Mn}, \text{Ru})$  expected for a ferromagnetic ordering of high-spin  $\text{Mn}^{3+}$  and low-spin  $\text{Ru}^{4+}$  moments in an atomistic picture. No lattice anomalies were observed in the studied temperature interval. These results are interpreted in terms of a strong Mn—Ru hybridization, which may freeze the orientation of the  $\text{Mn}^{3+} e_g$  orbitals as well as broaden the  $e_g$  valence band, possibly leading to carrier-mediated ferromagnetism.

## II. EXPERIMENTAL DETAILS

Polycrystalline samples with nominal composition  $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$  (LCMR),  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$  (LSMR), and  $\text{La}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$  (LBMN) were grown by conventional solid-state reaction, as described in Ref. 6. All measurements reported in this work were taken at the NIST Center for Neutron Research. The high-resolution NPD measurements were performed on the BT-1 powder diffractometer, using monochromatic beams with  $\lambda = 1.5402(1)$  Å and  $2.0783(1)$  Å produced by  $\text{Cu}(311)$  and  $\text{Ge}(311)$  monochromators, respectively. Collimations were  $15'$ ,  $20'$ , and  $7'$  arc before and after the monochromator, and before detectors, respectively. The intensities were measured in steps of  $0.05^\circ$  in  $2\theta$  range  $3\text{--}168^\circ$ . The samples were placed into cylindrical vanadium cans. Crystal and magnetic structure refinements were carried out using the program GSAS.<sup>7</sup> The nuclear scattering amplitudes are 0.827, 0.490, 0.702, 0.525,  $-0.373$ , 0.721, and  $0.581$  ( $\times 10^{-14}$  m) for La,

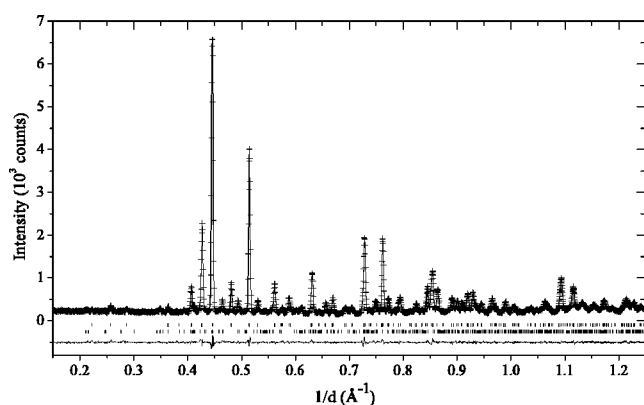


FIG. 1. Observed (cross symbols) and calculated (solid line) high-resolution neutron-diffraction intensities of  $\text{La}_{0.5+\delta}\text{Ca}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  at 300 K, taken with  $\lambda = 1.5402(1)$  Å. The difference profile is also given. Short vertical lines correspond to Bragg peak positions for the main phase (upper) and for the  $\text{LaCa}_2\text{RuO}_6$  impurity phase (lower).

Ca, Sr, Ba, Mn, Ru, and O, respectively.<sup>7</sup> For LCMR, an impurity phase of  $\text{LaCa}_2\text{RuO}_6$  (6.5% weight fraction) with monoclinic crystal structure ( $P2_1/n$  symmetry)<sup>8</sup> was detected, while for LBMR impurity phases of  $\text{Ba}_3\text{RuMn}_2\text{O}_9$  (Ref. 9) and  $\text{BaRuO}_3$  (Ref. 10) were identified with weight fractions of 5.8% and 1.5%, respectively. Such impurity phases were included in the refinements for the respective sample. For LSMR, some Bragg peaks remained unindexed, being ascribed to unidentified impurity phases. The intensity of the strongest of such peaks is 5% of the strongest peak of the main phase. The relatively poor fitting thus obtained for LSMR ( $\chi^2=3.1$ ) prevented a reliable refinement of some structural parameters of the main phase for this particular sample.

High-intensity NPD measurements were performed for LCMR at the BT-7 triple axis spectrometer operated on two-axis mode, using a monochromatic beam with  $\lambda = 2.465(1)$  Å produced by a pyrolytic graphite monochromator. Relaxed collimations were employed in order to optimize intensity, leading to an instrumental resolution in  $2\theta$  of  $\sim 1.0$ – $1.3^\circ$  full width at half maximum at the angular region of interest to this work. The sample was placed into an Al cylindrical can to minimize incoherent scattering by the sample holder. Both high-resolution and high-intensity data were collected at various temperatures in the range 10–300 K, employing closed-cycle He cryostats.

### III. RESULTS AND ANALYSIS

Figure 1 shows the observed NPD intensities of LCMR at room temperature (cross symbols). The crystal structure of this compound was refined using an orthorhombic perovskite model ( $Pnma$  symmetry), with Mn and Ru ions at the same crystallographic site, as well as La and Ca ions. The occupancies  $\nu$  were refined under the constraints  $\nu(\text{Ca}) + \nu(\text{Ba}) = 1$  and  $\nu(\text{Mn}) + \nu(\text{Ru}) = 1$ . Preliminary refinements showed the oxygen occupancy close to the stoichiometric value,  $\nu(\text{O}) = 3.00(2)$ . This parameter was then fixed at 3 in subse-

quent refinements in order to improve the stability of the fitting procedure. The calculated NPD intensities using the above model are given in Fig. 1 (solid line), yielding good fits to the observed intensities. The crystal structures of LSMR and LBMR were also refined using the same ionic-disordered model with  $Pnma$  symmetry used for LCMR. The refined structural parameters of LCMR and LBMR at 300 K are given in Table I, together with selected bond distances and bonding angles. The average  $B$ -O bond distance ( $B = \text{Mn, Ru}$ ) assumes nearly the same value,  $\sim 1.99$  Å, for both LCMR and LBMR. Also, the  $\text{BO}_6$  octahedra are nearly regular, since the  $B$ -O bond distances show only a small distribution in both samples, within  $\sim 0.02$  Å. The unit-cell volume shows a significant expansion for LBMR with respect to LCMR. This is accomplished by a rotation of the  $\text{BO}_6$  octahedra in order to increase the  $B$ -O- $B$  bonding angle, thus expanding the average Ba-O bond distances with respect to Ca-O. We note that the  $B$ -O1- $B$  angle increases from  $155.32(12)^\circ$  for LCMR to  $163.2(3)^\circ$  for LBMR, while the  $B$ -O2- $B$  angle experiences a more significant change, from  $155.51(7)^\circ$  for LCMR to  $175.5(4)^\circ$  for LBMR.

Figures 2(a) and 2(b) show the temperature dependence of the lattice parameters  $a$ ,  $b$ , and  $c$  and unit-cell volume for LCMR and LSMR, respectively. The lattice parameters show a conventional contraction with decreasing  $T$ , with no detectable anomaly in the studied temperature interval. The temperature dependencies of  $B$ -O bond distances and  $B$ -O- $B$  bonding angles for LCMR are given in Figs. 3(a) and 3(b), respectively. The  $B$ -O bond lengths remains nearly constant over the studied  $T$  interval, within  $\sim 0.005$  Å.

Figures 4(a) and 4(b) show a low-angle portion of the high-resolution neutron powder profile of LCMR, taken with Ge(311) monochromator at  $T=300$  K and  $T=10$  K, respectively, and the calculation according to the lattice model described above. Clearly, additional contributions to the intensities of the (101)/(020) and (200)/(121)/(002) Bragg peaks are observed at  $T=10$  K [see difference curve in Fig. 4(b)], arising from the ordering of the Mn(Ru) spins. The widths of the FM Bragg peaks are found to be instrumental only, thus FM domains are larger than  $\sim 500$  Å for all studied samples. Figure 4(c) shows a comparison between the observed profile at  $T=10$  K and a model including a ferromagnetic ordering for the Mn and Ru spins, yielding good agreement with each other.

Figure 5 shows the temperature dependence of the summed integrated intensity of the (101), (020), (200), (002), and (121) NPD Bragg reflections with significant FM contributions for LCMR and LSMR. Ferromagnetic ordering is observed below  $T_c \sim 200$  K for LCMR and  $T_c \sim 250$  K for LSMR, consistent with dc magnetization measurements previously performed in these samples.<sup>6</sup> Table II summarizes the magnetic properties of the studied samples, obtained from our refinements using high-resolution NPD data except where noted otherwise.

In order to search for weak magnetic signals not observable in high-resolution measurements, high-intensity energy-integrated NPD measurements were performed for LCMR. Figure 6(a) shows a portion of the neutron-scattering intensities at 13 K ( $\ll T_c$ ) subtracted by the intensities at 300 K ( $\gg T_c$ ). Besides the magnetic Bragg peaks already seen in the

TABLE I. Results of Rietveld refinements of neutron powder-diffraction data collected at 300 K for  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $\text{A}=\text{Ca}, \text{Ba}$ ). Refinements were carried out in space group  $Pnma$  (No. 62). Errors in parentheses are statistical only, and represent one standard deviation.

	A	Ca	Ba
$a$ (Å)		5.5099(2)	5.5975(5)
$b$ (Å)		7.7553(3)	7.9163(8)
$c$ (Å)		5.4819(3)	5.6197(8)
$\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}(x, 1/4, z)$			
$\delta$		0.056(12)	0.04(3)
$x$		0.0322(2)	-0.0069(14)
$z$		0.0067(4)	-0.0067(12)
$U_{iso}$ (Å <sup>2</sup> )		0.0120(4)	0.0101(9)
$\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}(1/2, 0, 0)$			
$\epsilon$		0.081(3)	0.024(3)
$U_{iso}$ (Å <sup>2</sup> )		0.009(2)	0.009 <sup>a</sup>
O1 ( $x, 1/4, z$ )			
$x$		0.4833(3)	0.502(2)
$z$		-0.0755(4)	0.0521(9)
$U_{11}, U_{33}$ (Å <sup>2</sup> )		0.0183(7)	0.034(2)
$U_{22}$ (Å <sup>2</sup> )		0.0068(10)	0.000(3)
O2 ( $x, y, z$ )			
$x$		0.2891(2)	0.252(3)
$y$		0.0387(2)	-0.0099(7)
$z$		0.2872(2)	0.252(3)
$U_{11}, U_{33}$ (Å <sup>2</sup> )		0.0147(3)	0.025(2)
$U_{22}$ (Å <sup>2</sup> )		0.0131(6)	0.018(3)
$U_{13}$ (Å <sup>2</sup> )		-0.0013(6)	0.012(2)
(Mn,Ru)-O1 (Å)		1.9847(5)	2.0006(7)
(Mn,Ru)-O2 (Å)		1.9796(11)	1.9845(3)
(Mn,Ru)-O2 (Å)		1.9970(12)	1.9846(4)
$\langle \text{Mn,Ru} \rangle$ -O (Å)		1.9871(6)	1.9899(3)
(Mn,Ru)-O1-(Mn,Ru) (°)		155.32(12)	163.2(3)
(Mn,Ru)-O2-(Mn,Ru) (°)		155.51(7)	175.4(4)
$Rp(\%)$		3.2	5.1
$wRp(\%)$		3.8	6.3
$\chi^2$		1.06	1.44

<sup>a</sup>Kept fixed at the same value found for  $\text{A}=\text{Ca}$  to avoid instabilities in the fitting procedure.

high-resolution measurements [see Figs. 4(b) and 4(c)], associated with a FM arrangement of (Mn,Ru) spins, no evidence for additional magnetic sublattices and/or competing magnetic structures or correlations were observed at low temperatures. Particularly, a chemical ordering of Mn and Ru ions in a double perovskite structure with either ferro- or ferrimagnetic spin arrangement at low temperatures would lead to magnetic contributions to the (110) and (011) Bragg peaks [arrow in Fig. 6(a)]. The absence of such a contribution in Fig. 6(a) demonstrates the absence of a significant volumetric fraction of the sample showing an ordered double perovskite crystal structure and contributing to the magnetism down to 10 K. In addition, no evidence of magnetic ordering in the impurity phases of this sample was observed.

Figure 6(b) shows a similar measurement at 230 K, therefore slightly above  $T_c \sim 200$  K, again subtracted by the scattering at 300 K. Significant short-range ferromagnetic correlations are observed at this temperature. From the widths of the broad structures centered at the positions where the FM peaks develop at low temperatures [solid line in Fig. 6(b)], a magnetic correlation length of 35(10) Å is found for LCMR at 230 K.

#### IV. DISCUSSION

Our results indicate that a FM state with a relatively low spontaneous moment [ $\sim 1.8\text{--}2.0\mu_B/(\text{Mn,Ru})$ ] is realized for  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$ ). No other co-

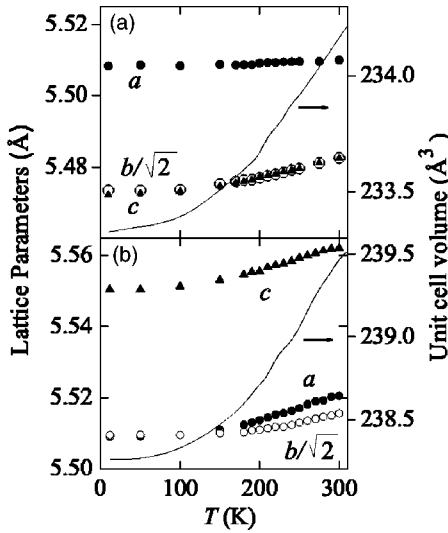


FIG. 2. Temperature dependence of the lattice parameters  $a$  (filled circles),  $b/\sqrt{2}$  (open circles), and  $c$  (filled triangles), and unit-cell volume (solid line) of (a)  $\text{La}_{0.5+\delta}\text{Ca}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$ , and (b)  $\text{La}_{0.5+\delta}\text{Sr}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$ .

existing magnetic sublattices were detected. In addition, this system does not display lattice anomalies that might be associated with orbital ordering, or volumetric changes at  $T_c$  due to an increase of the kinetic energy of  $d$  electrons in the FM phase, as observed in FM manganites without Ru substitution. We note that the system studied here is not metallic and does not show an appreciable change in conductivity at the onset of the FM phase.<sup>6</sup>

As a first step to rationalize the above observations, a discussion of the oxidation states of the Mn and Ru ions is worthwhile. Two possibilities arise from the charge neutrality condition for the formula unit: (i)  $\text{Mn}^{2+}-\text{Ru}^{5+}$ , and (ii)  $\text{Mn}^{3+}-\text{Ru}^{4+}$ . Based on our results, we argue against (i). In fact, the large differences between  $\text{Mn}^{2+}$  and  $\text{Ru}^{5+}$  in either electrostatic charge ( $3e$ ) and ionic radius ( $0.265 \text{ \AA}$ ) (Ref. 11) would most likely lead to a chemically ordered double per-

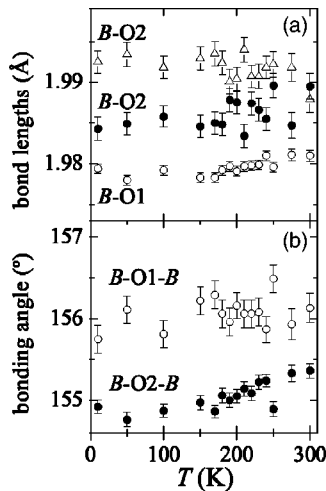


FIG. 3. Temperature-dependence of (a)  $B$ -O bond lengths ( $B=\text{Mn}, \text{Ru}$ ) and (b)  $B$ -O- $B$  bonding angles for  $\text{La}_{0.5+\delta}\text{Ca}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$ .

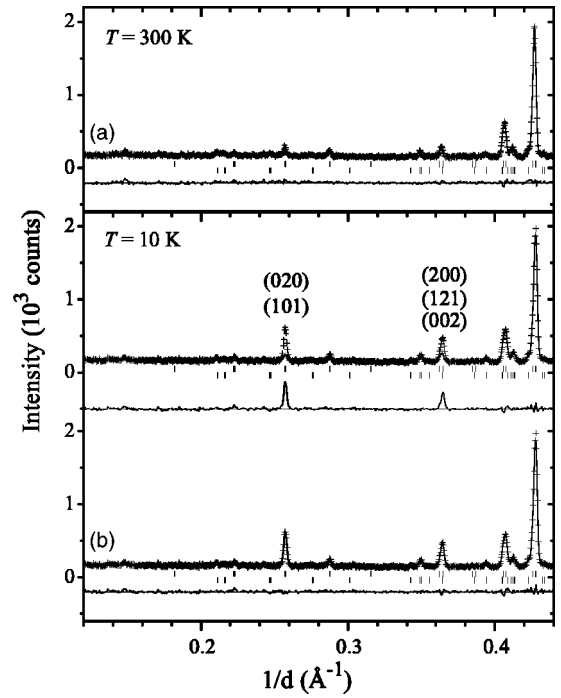


FIG. 4. Low angle portion of the observed high-resolution neutron-diffraction intensities of  $\text{La}_{0.5+\delta}\text{Ca}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  (cross symbols) at (a) 300 K and (b), (c) 10 K, taken with the Ge(311) monochromator. Calculated intensities (solid lines) are also given, for a nuclear-only model (a), (b), and for a nuclear + ferromagnetic model for the Mn and Ru spins (c). The difference profiles are also shown. Short vertical lines correspond to Bragg peak positions for the main phase (upper) and for the  $\text{LaCa}_2\text{RuO}_6$  impurity phase (lower).

ovskite structure.<sup>4</sup> Given the large differences between the nuclear neutron-scattering factors of Mn and Ru (with opposite signs, see Sec. II above), a significant volume fraction of such an ordered structure would be readily identified in our

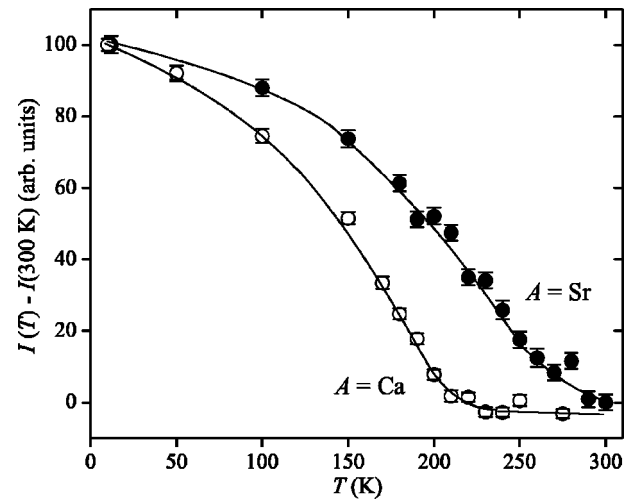


FIG. 5. Temperature dependence of the summed integrated intensity of the (101), (020), (200), (002), and (121) Bragg reflections which have significant contributions from a ferromagnetic spin arrangement of Mn and Ru spins. Solid curves are guides to the eye.



TABLE II. Summary of the magnetic properties of  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $A=\text{Ca, Sr, Ba}$ ) samples, obtained from the refinements of neutron powder-diffraction data.

A	Ca	Sr	Ba
Magnetic structure	Ferromagnetic	Ferromagnetic	Ferromagnetic
Ordered moments at 10 K	$1.77(2)\mu_B/(\text{Mn,Ru})$	$1.83(5)/(\text{Mn,Ru})$	$1.96(4)/(\text{Mn,Ru})$
$T_c$	$\sim 200$ K	$\sim 250$ K	$\sim 200$ K <sup>a</sup>

<sup>a</sup>Taken from Ref. 6.

NPD profiles, which was not the case (see Fig. 1). Even the presence of a significant volumetric fraction of short-range chemically ordered domains<sup>6</sup> is not consistent with our measurements. In fact, the magnetic state at low temperatures associated with such hypothetical clusters (either ferro- or ferrimagnetic) would lead to additional structures in our low-temperature NPD profiles, centered at positions such as  $(110)/(011)$  in Fig. 6. As a final argument against a significant presence of  $\text{Mn}^{2+}/\text{Ru}^{5+}$  pairs, the expected average  $(\text{Mn,Ru})\text{—O}$  distance for this configuration is  $2.10 \text{ \AA}$ ,<sup>11</sup> much larger than the observed values,  $\sim 1.99 \text{ \AA}$  (see Table I). We note that the average  $(\text{Mn,Ru})\text{—O}$  distance expected for  $\text{Mn}^{3+}/\text{Ru}^{4+}$  is  $2.03 \text{ \AA}$ ,<sup>11</sup> fairly close to the experimental values. The remaining discrepancy may be partly ascribed to a possible presence of a small fraction of  $\text{Mn}^{4+}$  or  $\text{Ru}^{5+}$  ions caused by off-stoichiometry effects ( $\delta, \epsilon \neq 0$ ). We should mention that superlattice Bragg reflections indicative of a chemically ordered double perovskite structure have been observed by electron diffraction for these same samples studied here.<sup>6</sup> Also, the crystal structure of

$\text{La}_{0.5+x}\text{Sr}_{0.5-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$  was found to show a transition from random to ordered distribution of Mn and Ru ions at  $x=0.0$ .<sup>12</sup> Nonetheless, our NPD results show that a chemically ordered state is not representative of the bulk of the LCMR, LSMR, and LBM samples studied in this work. A chemically disordered perovskite phase for LSMR was also reported by Horikubi *et al.*<sup>13</sup>

In view of the above, the  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $A=\text{Ca,Sr,Ba}$ ) compounds may be described as a random distribution of  $\text{Mn}^{3+}$  and  $\text{Ru}^{4+}$  ions in the  $B$  site of a perovskite structure. It is remarkable that a long-range FM state can survive to such a degree of random Ru substitution at the Mn site. We base our discussion upon a scenario proposed by Martin *et al.*<sup>3</sup> to explain the rapid quenching of the orbital-ordered state and the development of a FMM phase in  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  with relatively small levels of Ru substitution. According to this, the spatially extended character of the Ru  $4d$  orbitals would lead the  $4d:e_g$  states to participate in the band formation and contribute to make it broader, producing a FM coupling mechanism between mixed-valent Mn and  $\text{Ru}^{4+}$  ions based upon an enhancement of the double exchange interaction. We note that a broadening of the  $e_g$  band by Mn/Ru hybridization would lead to a FM coupling between Mn and Ru only if the  $e_g$  band is partially filled, i.e., the  $e_g$  density of states must be finite at the Fermi level. In the present case, our NPD measurements suggest that the Mn oxidation state is close to  $\text{Mn}^{3+}$  (see discussion above), with one  $e_g$  electron per Mn ion. In this case, the likelihood of  $e_g$  charge carriers increases with the ratio of the  $e_g$  bandwidth by the energy splitting. The presence of Ru ions is believed to increase the  $e_g$  bandwidth by Mn/Ru hybridization, and may decrease the Jahn-Teller splitting, since the local distortion of the  $\text{Mn}^{3+}\text{O}_6$  octahedra might be smoothed out by the chemical disorder. It is therefore not unreasonable to assume the presence of a significant  $e_g$  density of states at the Fermi level in  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $A=\text{Ca,Sr,Ba}$ ). If this assumption is correct, the above carrier-mediated mechanism for the FM coupling may be valid. We note that the possible presence of a small fraction of  $\text{Mn}^{4+}$  ions (see above) might create holes in the  $e_g$  band, favoring the FM coupling. We should mention that transport measurements do not show metallic behavior below  $T_c$ , although resistivity was found to be significantly low with a thermal behavior not characteristic of conventional semiconductors.<sup>6</sup> In fact, a presumably small carrier density combined with the strong chemical disorder of this system would make a metallic state highly unlikely even in the FM phase, due to Anderson localization. More direct investigations of the electronic structure of this system are required in order to confirm or dismiss the valid-

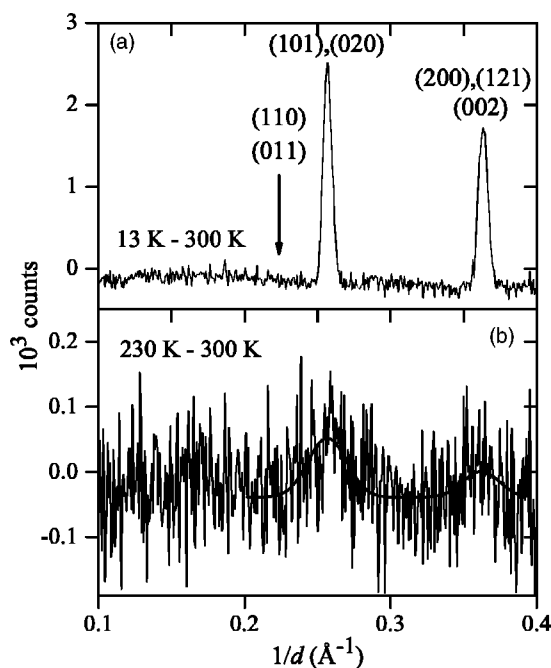


FIG. 6. High-intensity difference neutron profiles for  $\text{La}_{0.5+\delta}\text{Ca}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$ : (a)  $I(13 \text{ K}) - I(300 \text{ K})$ , and (b)  $I(230 \text{ K}) - I(300 \text{ K})$ , highlighting the magnetic scattering well below and slightly above  $T_c$ , respectively. The smooth solid line in (b) is a two-Gaussian fit to the experimental data.

ity of the above scenario. Notice that this is consistent with a previous report evidencing the presence of double exchange interactions in  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Ru}_x\text{O}_3$  up to large levels of Ru substitution ( $x \sim 0.4$ ).<sup>5</sup> We should mention that a FM  $\text{Mn}^{3+}$ - $\text{Ru}^{4+}$  superexchange interaction<sup>14</sup> is possibly another important ingredient that may lead to the robust ferromagnetism found in  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ ). On the other hand, the same values of  $T_c$  found for  $\text{A} = \text{Ca}$  and  $\text{A} = \text{Ba}$  (see Table II) despite the large differences in the  $(\text{Mn}, \text{Ru})$ - $\text{O}$ -( $\text{Mn}, \text{Ru}$ ) superexchange angles (see Table I) are intriguing, and suggest that superexchange alone is not sufficient to understand the magnetic properties of this system.

The ordered moments found at low temperatures ( $\sim 1.8$ – $2.0\mu_B/(\text{Mn}, \text{Ru})$ , see Table II) are significantly lower than the  $3\mu_B/(\text{Mn}, \text{Ru})$  expected for a FM arrangement of high-spin  $\text{Mn}^{3+}$  ( $4\mu_B$ ) and low-spin  $\text{Ru}^{4+}$  ( $2\mu_B$ ) moments in a spin-only atomistic picture. We first note that the Ru 4d states are highly hybridized with O 2p, which may reduce the Ru moments. We mention that  $\text{SrRuO}_3$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  are metallic ferromagnets with saturated magnetic moments well below  $2\mu_B/\text{Ru}^{4+}$ .<sup>15,16</sup> Second, the random distribution of Mn and Ru ions in the lattice might lead to some sites with frustrated exchange interactions in the FM lattice, leading to local spin reversal and/or loss of spin collinearity. A combination of the two effects above may lead to the reduced FM moments observed by NPD.

In transition-metal compounds with a significant density of degenerate  $t_{2g}$  and  $e_g$  orbitals, strong tendencies for orbital ordering (OO) have been identified.<sup>17</sup> The spin states associated with OO are generally antiferromagnetic, therefore OO and ferromagnetism (satisfying double exchange interactions) tend to be competing ground states. Such a competition is believed to be a decisive ingredient leading to the rich phase diagram observed in manganites, in addition to tendencies for charge ordering for specific concentrations of  $e_g$  electrons, which also favors OO. In the present case, the FM coupling is believed to arise from hybridization between  $\text{Mn}^{3+}$  and  $\text{Ru}^{4+}$   $e_g$  states, leading to a presumably small but significant carrier density in the  $e_g$  band. One might suspect that tendencies for OO should overcome the FM coupling in  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ ), since both

$\text{Mn}^{3+}$  and  $\text{Ru}^{4+}$  ions show degenerate  $d$  orbitals. However, the FM ground state actually observed in this system, with no cooperative distortions of the  $(\text{Mn}, \text{Ru})\text{O}_6$  octahedra (see Table I) and/or lattice anomalies that might be associated with OO (see Figs. 2 and 3), contradicts such an expectation, indicating that Ru substitution actually inhibits OO. In fact, previous studies indicate that even a light Ru substitution quenches orbitally ordered states in half doped manganites.<sup>3</sup> The most likely explanation for this tendency stems from the spatially extended character of the Ru 4d states: the  $\text{Mn}^{3+}$   $e_g$  orbitals would have a tendency to point along the neighboring Ru ions, in order to take full advantage of the strong Mn-Ru hybridization.<sup>3</sup> Notice that each  $\text{Mn}^{3+}$  ion has two Mn/Ru neighbors along each binding direction. Thus each  $\text{Mn}^{3+}$   $e_g$  orbital would point to the direction with most Ru ions. This effect may freeze the orbital degree of freedom of  $\text{Mn}^{3+}$   $e_g$  and possibly  $\text{Ru}^{4+}$   $t_{2g}$  electrons. In a crystal structure with a random distribution of Ru and Mn ions (see Sec. III), long-range OO would be prevented, leading to an orbital glass state.

In conclusion, our NPD results on  $\text{La}_{0.5+\delta}\text{A}_{0.5-\delta}\text{Mn}_{0.5+\epsilon}\text{Ru}_{0.5-\epsilon}\text{O}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ ) show a perovskite crystal structure with no chemical ordering of  $\text{Mn}^{3+}$  and  $\text{Ru}^{4+}$  ions. No evidence of long-range orbital ordering was observed, possibly due to a freezing of the orbital degree of freedom caused by a significant Mn-Ru hybridization. A long-range FM spin structure was observed. This result was ascribed to the spatially extended character of Ru 4d levels, contributing to broaden the  $e_g$  band and leading to the presence of a small but finite density of  $e_g$  states at the Fermi level. Such states may lead to carrier-mediated FM coupling. In this context, the nonmetallic conductivity observed in this system<sup>6</sup> was ascribed to Anderson localization caused by the large Ru/Mn chemical disorder.

## ACKNOWLEDGMENTS

Work at the University of Maryland was supported by NSF-MRSEC Contract No. DMR 00-80008. This work was also supported by Fapesp and CNPq, Brazil, and DST, New Delhi, India.

\*Electronic address: egranado@ifi.unicamp.br

<sup>1</sup>P. V. Vanitha, A. Arulraj, A. R. Raju, and C. N. R. Rao, C.R. Acad. Sci., Ser. IIC: Chim **2**, 595 (1999).

<sup>2</sup>A. Maignan, C. Martin, M. Hervieu, and B. Raveau, Solid State Commun. **117**, 377 (2001).

<sup>3</sup>C. Martin, A. Maignan, M. Hervieu, C. Autret, B. Raveau, and D. I. Khomskii, Phys. Rev. B **63**, 174402 (2001).

<sup>4</sup>For a review, see M. T. Anderson, K. B. Greenwood, G. A. Taylor, and K. R. Poeppelmeier, Prog. Solid State Chem. **22**, 197 (1993).

<sup>5</sup>S. S. Manoharan, R. K. Sahu, M. L. Rao, D. Elefant, and C. M. Schneider, Europhys. Lett. **59**, 451 (2002).

<sup>6</sup>K. Ramesha, V. Thangadurai, D. Sutar, S. V. Subramanyam, G. N.

Subbanna, and J. Gopalakrishnan, Mater. Res. Bull. **35**, 559 (2000).

<sup>7</sup>C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR086-748, 1990.

<sup>8</sup>P. D. Battle, J. B. Goodenough, and R. Price, J. Solid State Chem. **46**, 234 (1983).

<sup>9</sup>S. Frenzen and H. Mueller-Buschbaum, Z. Naturforsch., B: Chem. Sci. **50**, 585 (1995).

<sup>10</sup>S.-T. Hong and A. W. Sleight, J. Solid State Chem. **128**, 251 (1997).

<sup>11</sup>R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr. **A32**, 751 (1976).

<sup>12</sup>M. Fang, M. Kato, K. Yoshimura, and K. Kosuge, J. Alloys

- Compd. **317-318**, 136 (2001).
- <sup>13</sup>T. Horikubi, T. Mori, H. Nonobe, and N. Kamegashira, J. Alloys Compd. **289**, 42 (1999).
- <sup>14</sup>C. Martin, A. Maignan, M. Hervieu, B. Raveau, and J. Hejmanek, Eur. Phys. J. B **16**, 469 (2000).
- <sup>15</sup>J. J. Randall and R. Ward, J. Am. Chem. Soc. **81**, 2629 (1959).
- <sup>16</sup>M. K. Crawford, R. L. Harlow, W. Marshall, Z. Li, G. Cao, R. L. Lindstrom, Q. Huang, and J. W. Lynn, Phys. Rev. B **65**, 214412 (2002).
- <sup>17</sup>For a review, see Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).